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FINAL REPORT

Rapid Solidification Processing of Composites

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1 Introduction

The object of this research was to investigate new methods for the high-speed fabrication of metal-matrix composites. These composites can operate at higher temperatures than the more established fiber/epoxy composites. Rapid Solidification Technology (RST) holds much promise for the production of metal matrix-composite materials. The time for which the different phases of the composite are in contact at high temperature is limited to milliseconds. Combinations of materials can, therefore, be used, which would react or degrade when held at these temperatures for the length of time required to form composites by conventional techniques. Rapid quenching to room temperature also allows the production of matrix alloys with non-equilibrium concentrations of elements. Subsequent segregation may improve matrix properties [1] or improve the integrity of the bond at the matrix/reinforcement interface [2]. Additionally, RST is a commercially viable method for producing amorphous alloys in large volumes.

In this discussion of rapidly solidified composite materials, both the so-called *in situ* composites, and those composites which consist of a rapidly solidified matrix or reinforcement, which is then formed into a composite material using traditional processes, are excluded from consideration. For example, rapidly solidified Al-Li-Mg-Cu-Zr alloys may be aged to produce cored, or "composite," precipitates [3]. While these precipitates, which consist of Al_3Li around a Zr-rich core, may be composite precipitates, the material is not what is usually considered a composite material. Similarly, rapidly solidified Ti-Al ribbon may be reinforced with carbon fibers [4] by stacking alternating layers of the Ti-Al ribbons and the carbon fibers, and subsequently pressing the stack in an evacuated furnace to cause the metal to flow superplastically around the fibers. Although the matrix has been rapidly solidified, the composite has not. Thus, our examination is restricted to those materials with introduced dissimilar phases which are present at the time of rapid solidification.



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Defined this way, materials are possible with all the advantages listed above. The work that has been done with these materials falls into two major categories. First, there are the laminated rapidly solidified composites, which are comprised of bonded dissimilar rapidly solidified metallic ribbons. Second, there are the reinforced rapidly solidified composites, in which some reinforcing medium is embedded in the rapidly solidified metallic ribbon. (Reinforcement is simply a convenient term—it may be that the purpose of the included material is not to reinforce, but, for example, to alter the wear characteristics.) There are two classes of reinforcing media—discrete, or particulate; and continuous, or filamentary

2 Laminated Rapidly Solidified Composites

One type of rapidly solidified (RS) composite is the laminates. These composites consist of several layers of rapidly solidified metal which bond together in the casting process. Thus, the advantages of rapidly solidified alloys are combined with the advantages of a bimetallic (or even multilayered) form. Casting the composite as a whole has advantages over casting each alloy separately and subsequently processing them into a composite. For example, composites containing amorphous alloys that crystallize at temperatures below those used in traditional composite forming processes could be produced.

The first laminated rapidly solidified composite [5] was produced with a double roller rapid solidification apparatus in which the second layer of metal was ejected upon the first (Fig. 1). It was thought that the thermal contact between the ribbon and a single roller would be insufficient to allow the requisite thermal conduction necessary for producing an amorphous alloy ribbon. The distance from each crucible of molten alloy to the nip of the rollers was selected so that the first alloy ribbon was solid before the second alloy melt was cast onto it, and both ribbons were solid before they reached the nip of the rollers. Experiments were performed in which a single ribbon was cast to find the distance (and thus, for a given roller speed, the time) required for each alloy to be solidified. The alloys

were still very hot when the nip of the rollers was reached, so good bonding occurred between the ribbons. It was necessary to take care, however, not to place the crucibles so close to the roller nip that the ribbons were very near their melting point when it was reached. Failure to take this precaution would result in a boundary between the alloy layers which was not sharp.

Several combinations of laminated ribbons were produced with this apparatus [6]: a narrow $\text{Pd}_{80}\text{Si}_{20}$ ribbon was bonded upon a wider $\text{Ni}_{59}\text{Fe}_{19}\text{Si}_8\text{B}_{14}$ ribbon, a $\text{Co}_{75}\text{Si}_{10}\text{B}_{15}$ ribbon was bonded upon an $\text{Ni}_{75}\text{Si}_{10}\text{B}_{15}$ ribbon, and a $\text{Pd}_{83.5}\text{Si}_{16.5}$ ribbon was bonded upon an $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$ ribbon. Both layers were amorphous in these cases, as determined by X-ray diffractometry. Differential Thermal Analysis (DTA) showed that the crystallization temperatures were the same as those of the individual alloys, which suggests that no significant amount of a third alloy had formed. X-ray microanalysis was used to determine that the boundary between the alloy ribbons was sharp. In bending tests, these laminates could be bent 180° without separation. Another laminate, Permalloy $\text{Fe}_{55}\text{Ni}_{45}$ upon $\text{Pd}_{80}\text{Si}_{20}$ also had a sharply defined boundary between the constituent layers and could be bent 180° . This laminate, however, had a crystalline layer (the Permalloy) bonded to an amorphous layer. While an attempt was made to bond $\text{Fe}_{55}\text{Ni}_{45}$ upon $\text{Co}_{75}\text{Si}_{10}\text{B}_{15}$, the layers of this laminate had a sharply defined boundary but separated upon bending to 180° .

It is, however, possible for composites to be rapidly solidified on a single chill roller [7]. Both amorphous and amorphous/crystalline composites were produced using a single chill roller, much the same as the double roller method examined above, except that the alloys were allowed to bond without the aid of the mechanical pressing of the second chill roller (Fig. 2). This was accomplished by selecting the roller surface speed and the distance between crucibles such that the first alloy was still a liquid when the second alloy was ejected onto it. Thus, the first alloy must be a highly viscous liquid at the time

of second alloy deposition so that mixing between the two layers will be minimized. The technique was demonstrated in an entirely amorphous system by casting a narrow $\text{Pd}_{80}\text{Si}_{20}$ ribbon upon a wider $(\text{Ni}_{0.75}\text{Fe}_{0.25})_{78}\text{Si}_8\text{B}_{14}$ ribbon. A wide $(\text{Ni}_{0.75}\text{Fe}_{0.25})_{78}\text{Si}_8\text{B}_{14}$ ribbon was cast onto a narrow phosphor-bronze alloy ribbon to demonstrate this technique with an amorphous/crystalline system. As before, DTA, X-ray diffraction, X-ray profiling, and backscattered electron imaging were used to demonstrate that the alloys were not mixed at the interface (*i.e.*, the boundary between the constituent ribbons was sharp) despite the fact that the boundary was mechanically strong. It was found that the parameter most important to producing a uniform composite ribbon was the temperatures of the melts, and thus the relationship between the roller speed and the distance between crucibles. Other parameters, such as the stand-off distance of the crucible nozzles from the chill roller were also important, but less so. If, for example, the nozzles were too close to the roller (<0.1 mm), the flow of the alloy ejected upstream disturbed that of the alloy ejected downstream, while if they were too far (>0.5 mm), the surface of the composite was rough.

A modification of this technique [6] in which the molten alloys were ejected onto a Be-Cu belt that ran over two rollers (Fig. 3) was used to prepare a laminate of an $\text{Fe}_{75}\text{Si}_{10}\text{B}_{15}$ ribbon upon a $\text{Pd}_{83.5}\text{Si}_{16.5}$ ribbon. This modification is especially useful if one does not want to introduce a curvature into the composite due to the shape of the roller. Both layers of metal remained amorphous in this experiment, and the boundary between them was sharp. Some separation occurred in a 180° bending test, but none was observed when the laminate was wound around a 5 mm rod.

An interesting application of the single chill surface technique [8] has been used to solve the problem of brittleness in melt-spun semiconducting material. Melt-spinning semiconductors has been considered a low-cost route to photovoltaics, but in practice the semiconducting ribbon produced has been too brittle and of too small a grain size for practical applications. However, the problem of brittleness has been circumvented by casting

a rapidly solidified laminate consisting of a metal bottom layer and a semiconducting top layer. The technique was demonstrated by casting InSb on top of amorphous $\text{Cu}_{50}\text{Zr}_{50}$, on the inside of a chill drum (Fig. 4). While the boundary was sharp, there were some entrapped gasses at the interface, as the process was not carried out in vacuum.

Another study [9] has been done involving both laminated composites and "incremental casting" of layers of the same alloy, which, although it does not produce a composite, points out some issues important to the production of laminated composites. The goal in these experiments was to produce an amorphous ribbon much thicker than previously possible, by casting up to five ribbons upon one another. When all the ribbons were of the same material, a single crucible with several nozzles, only about 3 mm apart, was used. When casting a crystalline Ni-based superalloy, epitaxy was found between the grains in each layer cast. Casting a two layer amorphous $\text{Ni}_{40}\text{Fe}_{40}\text{B}_{20}$ ribbon was done so successfully that no boundary could be observed between the individual layers. When casting a four-layer ribbon from a single nozzle, letting the ribbon wrap itself around the chill roller for additional layers to be added, poor bonding was found between the third and fourth layer, and some crystallization was found at the interfaces. These layers were each quite thick ($\approx 50 \mu\text{m}$) and thus contained too much heat to be conducted away in the short time necessary to prevent crystallization. Magnetic coercivity measurements revealed that some degree of crystallization had occurred, even in ribbons that had no observable crystallites. This is not a problem unique to multiple layers of the same alloy, but must also be considered when attempting to cast a multilayered composite. Finally, an experiment was performed which demonstrated that the top of a ribbon can be deformed by the next ribbon cast onto it. A narrow stream of $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$ was cast onto a much wider ribbon, and the result was not a thicker piece where the narrow stream was directed, but, instead, a groove due to its deformation of the first ribbon (Fig. 5).

An interesting variation on this technique [10] can be used to create a composite in which the individual ribbons are not bonded face to face, but edge to edge. In this scheme,

the crucibles do not cast each subsequent ribbon on top of the previous one, but, rather, to the side of the previous one (Fig. 6). Bonding is at the edge contact. The boundary zone between the ribbons is not necessarily sharp, and, from hardness data, may be as much as 1 mm wide. This technique may be used to make wide ribbons of the same material, or composites, limited only by the width of the chill surface.

Spray forming [11] offers another route to laminated rapidly solidified composites. It is a method similar to that used for the production of rapidly solidified alloy powders, except that the trajectory of the metal droplets is interrupted by a substrate to form a cohesive deposit as they solidify, instead of cooling to a solid before they are collected (Fig. 7). It would be very easy to spray deposit additional layers onto a strip formed by a spray rolling technique. As each particle undergoes rapid solidification upon striking the layer before it (or the substrate, if it is the first layer), there should be no alloying at the interface, and a sharp boundary should be the result.

3 Discretely Reinforced Rapidly Solidified Composites

There are two major methods for the preparation of particle-reinforced composite materials. One may place the particles in the melt while it is held in the crucible, where they will be distributed by either the stirring action of the induction heater, or by a stirring apparatus, before ejection onto the chill roller. Alternatively, one may inject the particles into the melt puddle while it is still liquid on the chill roller. In this case the particles are distributed by the flow of the liquid matrix material in the puddle and by the continuous addition of particles as the ribbon is produced. A third method, in which the particles are injected into the melt in the crucible just before it is ejected onto the chill roller, may be viewed as a modification of either of the two methods above, depending on whether one is concerned with where the particles are added or when they are added.

The simplest and, therefore, the first method [12] used to prepare particle-reinforced rapidly solidified composite materials is simply to add reinforcing particles to the melt before it is ejected onto the chill roller (Fig. 8). Although the particles may be dispersed through the melt by means of an agitator, the particles may be kept dispersed by the stirring action of the induction coils used to heat the melt, if the particles' density is not too different from that of the melt.

In practice, using MoB_2 particles and an $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ matrix, it was found that many particles in the ribbon protruded from the top surface, while none were found at the surface that had been in contact with the chill roller, although the particles were well dispersed in the melt. This phenomenon was later determined [13] to be a result of turbulence in the melt puddle. Such a particle distribution was considered an advantage, as it made it possible for the strip to be used as an abrasive tool, the hard particles being firmly embedded in the matrix despite their protrusion. It is interesting that the particles, in this case, were formed in the melt by adding Mo and B in the proper stoichiometric ratio at 1773 K, the temperature at which MoB_2 forms but remains dissolved, and reducing the temperature to 1383 K, causing the MoB_2 to precipitate out in the form of particles. The particle size could be controlled by adjusting the cooling rate. Rapid quenching from 1383 K resulted in a thin $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ ribbon with MoB_2 particles evenly distributed and firmly embedded in one surface. Some requirements should be noted for this sort of scheme to work with other alloy systems. Wetting of the particles by the melt is not necessary, but facilitates processing. The particles ought not react with the melt at the processing temperature. Obviously, the particles must not be of a lower melting temperature than the melt, which may be a severe restriction.

Much work has been done with WC as the reinforcing particles, as they are hard and have a very high melting point (3143 K). The effect of adding 4–5 μm WC particles to molten $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ on the tensile yield stress of the resulting ribbon has been investigated

[14]. For ribbons containing about 7% WC particles by volume, it was found that these particles were distributed uniformly throughout the matrix. Some crystallization of the matrix was induced by the particles, as a crystalline metastable phase was observed at the interface between the matrix and some of the particles.

The presence of WC particles in ribbons was observed to improve the mechanical properties over those of an unreinforced $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ ribbon. The reinforced ribbon could be bent 180° without fracturing and the yield stress was 1.4 times that of the unreinforced metal (280 kg/mm^2 compared to 203 kg/mm^2). This is near the theoretical upper bound of a predicted increase, based on an assumption of approximate proportionality between the Young's Modulus and the yield stress of an amorphous material, and the linear rule of mixtures which assumes equal strain in both the matrix and the reinforcement phases. A lower bound is set by a model which assumes equal stress in both the matrix and reinforcement. Thus, a small volume fraction of particles can make a large difference between the yield stress of the composite and that of the unreinforced matrix material.

The upper bound for the expected Young's Modulus of a composite is found by assuming that the reinforcement and the matrix are parallel elements subject to the same strain [15]. The result of this assumption is that

$$E_c = E_m(1 - V_r) + E_r V_r \quad (1)$$

where E_c , E_m , and E_r are the Young's Moduli of the composite, the matrix material, and the reinforcing material, respectively, and V_r is the volume fraction of the reinforcement. This is often called the linear rule of mixtures. A lower bound is calculated by assuming that the reinforcement and the matrix are serial elements, and thus are subject to the same stress. This assumption leads to the relationship

$$E_c = \frac{1}{(1 - V_r)/E_m + V_r/E_r} \quad (2)$$

which is appropriate when the reinforcement is poorly bonded to the matrix material, while the assumption of equal strain is more appropriate for a well bonded composite.

The yield stress of an amorphous alloy has been observed [16] to be roughly proportional to the Young's Modulus, which may lead one to expect that the yield stress of a reinforced amorphous alloy may be predicted from the Young's Modulus derived via the linear rule of mixtures. Although both the Young's Modulus and the yield stress of these composites appear to follow the linear rule of mixtures, theory [17] indicates that, in the case of the yield stress, this is simply fortuitous. This theory also indicates that the linear rule of mixtures is obeyed by Young's Modulus only when it is determined at low stresses, is due to the fact that the length and diameter of a particle are comparable. An elementary analysis shows that efficient stress transfer from the matrix to an element of reinforcement requires this element to have a length:diameter ratio that exceeds some critical value, as some finite length is required for the full transfer of stress if the maximum shear stress of the matrix is not to be exceeded. The critical aspect ratio is equal to the fracture strength of the reinforcing element divided by twice the maximum shear stress of the matrix. Typically, the value of this ratio is about ten.

The particles reinforcing these rapidly solidified materials have an aspect ratio of about unity, so the full stress on the matrix can not be transferred to the reinforcement through the interface. It may be expected that the linear rule of mixtures will be obeyed by the Young's Modulus only up to the low stress that may be transferred without exceeding the maximum shear stress of the matrix. An improvement of the yield stress brought about by the presence of particles should not be expected at all. The observed improvement must, then, be brought about by some mechanism other than the transfer of stress from matrix to reinforcement. This mechanism may be that of work hardening by geometrically necessary dislocations [18] introduced to accommodate the differences in deformation behavior between the matrix and the reinforcing material. The additional stress required to generate

these dislocations increases the yield stress of the composite. There is, however, no reason to expect this increased yield stress to obey the linear rule of mixtures. Although this theory was developed for crystalline matrices, it can be legitimately applied to amorphous matrices as well [18], as the deformation takes place locally in a shear band that is narrow compared to the particle diameter.

This empirical effect was verified in studies of the effect of volume fraction of reinforcing 4–5 μm WC particles on the mechanical properties of $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ [15, 20]. It was shown that both the yield stress and the Young's Modulus increase essentially according to the upper bound set by the linear rule of mixtures, up to 18.2% (by volume) of particles, which was the limit of the study. At this point, the Young's Modulus (as determined by an ultrasonic method) was 2.2 times that of the unreinforced alloy (Fig. 9). An implication of this behavior of the Young's Modulus is that there is excellent bonding between the particles and the matrix, and thus complete transference of stress and strain between them without debonding at the low stress levels produced by the ultrasonic method used in the study. This is not surprising, as WC is wetted by liquid Ni, the primary component of the melt. Examination of the slip bands in specimens plastically deformed in bending tests revealed that, up to a particle volume fraction of about 7%, the bands are straight and bypass the particles. At higher volume fractions the slip bands appear more complex—they occur in sets near the particles, and are of many different orientations. These observations are explained by a bypass mechanism, in which plastic deformation occurs solely in the matrix.

The effect of much smaller (0.6 μm) WC particles on Ni-based amorphous alloys has also been investigated [21]. Ribbons were prepared by, again, adding WC particles to the molten $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ and $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ in volume fractions up to 15%. These particles were uniformly distributed and had the same effect on the Young's Modulus and the yield stress as the larger particles had, namely, that the mechanical properties were improved

according to the linear rule of mixtures. The small size of the particles improved the composite's ductility, however, increasing the volume fraction of WC at which the ribbons may be bent back 180° without decohesion from 6% to 10%.

Additionally, these smaller particles were used to reinforce both amorphous $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ spheres and $(\text{Ni}_{0.78}\text{P}_{0.12}\text{B}_{0.10})_{98}\text{Al}_2$ wires. The spheres were produced by ejecting the melt into a rotating water bath in which the parameters were controlled so that the flow was laminar, which produces spheres with a median diameter larger than that of the nozzle hole (Fig. 10). In this case an $80\text{ }\mu\text{m}$ orifice was used to produce spheres having a median diameter of $174\text{ }\mu\text{m}$ and containing 4% WC by volume. For comparison, unreinforced spheres had a median diameter of $98\text{ }\mu\text{m}$. The fact that the median particle sizes are larger than the nozzle hole is evidence that the flow was, indeed, laminar, as turbulent flow results in particles smaller than the hole diameter. Additionally, it should be noted that the particle size distributions were normal in both cases, although the distribution was wider in the case of the reinforced material. This difference may be explained as an increased kinematic viscosity of the melt caused by the presence of particles, and thus is not necessarily a result of a difference in the process of solidification.

The reinforced wires were cast by conventional in-rotating-water spinning, at up to 4% WC by volume. As was the case with the reinforced ribbons, the Young's Modulus was improved, and the yield stress was increased in accordance with the linear rule of mixtures.

Other properties besides the mechanical can be affected by the inclusion of particles in an amorphous matrix. The effect on the magnetic properties of the magnetic tape head material $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ were examined [22] by the addition of up to 2% $2\text{--}3\text{ }\mu\text{m}$ WC particles by volume. Note that WC is well wetted by liquid Co. Unreinforced alloys were made under exactly the same conditions for comparison, on a single chill roller. No reaction occurred between the particles and the melt, and no other phases were found at the particle/matrix interface. Both the apparent saturation magnetic induction and the Curie

temperature showed little change from that of the unreinforced material, certainly no more than would be predicted by considering that the matrix volume fraction has been reduced from 100% to 98%. Additionally, comparing the reinforced alloy to an alloy in which WC had been dissolved (which causes a significant reduction in the Curie temperature) demonstrated that no WC had dissolved in the matrix. The effective permeability was also investigated both as a function of annealing temperature at 10 mOe and 1 kHz and as a function of frequency at 10 mOe after annealing for 5 min at 723 K. Both the reinforced and the unreinforced materials showed the same effective permeability after having been annealed at various temperatures—the effect was that it was reduced except for annealing at temperatures just above the Curie temperature. The reinforced material, however, showed a 20–40% improvement in effective permeability at frequencies greater than 10 kHz compared to the unreinforced samples, each of which had been annealed for 5 min at 723 K (which is just above the Curie temperature) (Fig. 11). This suggests that the WC particles may reduce domain size, and thus also reduce eddy current losses during high frequency magnetization.

Oxide particles of Cr_2O_3 and ZrO_2 are not well-wetted by $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ alloy, but composite ribbons were produced [23] anyway by adding the particles, not to the melt, but to the melt stream of a conventionally-cooled molten ingot as it was poured. This ingot was then re-melted in a crucible for the melt-spinning of a rapidly solidified composite on a single chill roller. The particles dissolved to some extent in the alloy during the conventional cooling. Thus, the particles included in the ingot were very fine. In this experiment, the Cr_2O_3 particles were reduced in diameter from $1\text{ }\mu\text{m}$ to an average of $0.0618\text{ }\mu\text{m}$, while the ZrO_2 particles went from $1\text{ }\mu\text{m}$ to an average of $0.0562\text{ }\mu\text{m}$ due to the outer portions being dissolved. There was, however, no detectable size difference between the particles in the crystalline ingot and those in the melt-spun amorphous ribbon, indicating that no further dissolution took place during the re-melting. The volume fraction of particles in these experiments was very low: only 0.76% for Cr_2O_3 particles or 0.52% for ZrO_3 particles.

This technique succeeded in producing an amorphous ribbon which included very fine non-wetted particles, which would have floated and agglomerated if simply added to the melt before melt-spinning.

Not only does the inclusion of particles affect the properties of the amorphous matrix of the composite, but it may also affect the crystallization process of the matrix [24], which could have important technological ramifications. The effect of particles on the crystallization process has been investigated by adding 1 μm sized WC to melt-spun $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$. The WC was kept dispersed by induction stirring. The resulting composites ranged from 2 to 12% in volume fraction of WC. Differential Scanning Calorimetry, Transmission Electron Microscopy, and X-Ray Diffractometry studies led to the conclusions that the activation energy for crystallization was reduced with increasing volume fraction of WC, that crystallization proceeds more rapidly in reinforced composites than in the unreinforced counterpart, and that the presence of WC particles may alter the crystallization mechanism from one of nucleation and growth to one of growth of embryos containing a WC particle.

Graphite particles have been embedded in a melt-spun LM-13 Al-Si alloy [25] by adding particles to the melt. This composite was investigated as it may have desirable wear characteristics. The volume fraction of graphite was not reported, but it was observed that the inclusion of the graphite did not affect the microstructure. Comparison with Al-Si material produced in the same manner, but without the graphite particles, showed that there was no difference in either the spacing of the dendritic α -Al arms or the size and shape of precipitated Si particles.

The other method of introducing particles into a rapidly solidified ribbon, injecting them into the melt puddle after the metal is ejected from the crucible is not quite so simple as adding them to the melt in the crucible and, therefore, has not been practiced for as long. This method [26, 27] consists of adding the particles to a stream of gas flowing between

the nozzle and the chill roller, thus injecting them into the melt just before solidification (Fig. 12). The flowing gas has the added effect of stabilizing the quenching of the metal, as the turbulence in the boundary layer at the roller's surface is reduced. This technique was demonstrated using He gas to embed WC, TiC, and Mo particles in amorphous $\text{Ni}_{80}\text{Si}_{14}\text{B}_6$, WC and TiC particles in amorphous $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$, and WC in polycrystalline Sn ribbons. It was discovered that the volume fraction of embedded particles increased linearly with the pressure of the gas stream, once a certain critical pressure had been reached. The results of these demonstrations were ribbons with up to 7% particles by volume homogeneously distributed throughout. Attempts to increase the volume fraction of particles beyond this point by further increasing the gas stream pressure resulted in a lower volume fraction and a poor ribbon surface quality, due to gas pockets formed at the ribbon/chill roller interface during melt-spinning. It should be noted that homogeneity can be improved by pre-heating the particles to prevent them from forming clumps in the ribbon.

Particles introduced into a rapidly solidified ribbon in this fashion had the same effect on its mechanical properties as particles introduced by mixing them into the melt [19], namely, that the Young's Modulus and the yield stress increased in accordance with the linear rule of mixtures. It was found, for example, that a volume fraction of 6.7% WC in $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ increased both its Young's Modulus and its yield stress by a factor of about 1.4.

Experiments with larger particles, however, showed that the wettability of the particle by the liquid matrix material determines the effect that the inclusion of particles has on the mechanical properties of the ribbon [28]. Various kinds of particles ($17\text{ }\mu\text{m}$ and $70\text{ }\mu\text{m}$ SiC, plain and coated with $2\text{ }\mu\text{m}$ of Ni, and $100\text{ }\mu\text{m}$ B_4C) were injected into the melt puddle of an $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ alloy. Tensile tests performed to determine the yield stress showed that the particles that were well-wetted by the matrix (the Ni-coated SiC) could increase the yield stress by 20–30%. Particles that were not well-wetted (plain SiC and B_4C), however,

actually reduced the measured yield stress by about 25%. This is due to a difference in the deformation mechanisms between the ribbons with wetted particles and those with unwetted particles. When the particles are wetted, one expects the propagating slip bands to initiate cracking along themselves and across the particles. Unwetted particles, however, have pores at their particle/matrix interface which can concentrate stress when a slip band arrives at the particle. This stress is relieved by the formation of new slip bands. Thus, the pores grow rapidly and degrade the mechanical properties of the composite.

Because the particles are not in contact with the melt, except for the very short time before it solidifies, it is even possible to use particles having a melting point below the temperature of the melt [29]. For example, this technique has been used to add Ag particles to $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$. In this case, some Ag was dissolved in the ribbon before solidification took place, but Ag particles could still be found in the ribbon, though, no doubt, reduced in size.

Even more dramatic differences in materials may be accommodated using this technique. Polycrystalline aluminum ribbon containing a uniform dispersion of polystyrene spheres has been produced [30] in an attempt to increase the mechanical damping. In this work, however, it was impossible to determine whether the shrunken spheres observed were still polystyrene or had been charred into carbon, and the volume fraction of particles was so low that no measurable effect on the damping could be expected.

Spray forming [11], which has been suggested for the production of RS laminates, may also be used for the production of discretely reinforced composites. This approach has been investigated by embedding SiC particles and graphite flakes in an Al-5Si matrix. The composite was produced by adding the particles to the gas stream that carried them in molten form to the chill surface. The graphite flakes were observed to be in good interfacial contact with the SiC particles.

4 Continuously Reinforced Rapidly Solidified Composites

Reinforcing a rapidly solidified material with continuous wires or fibers raises the prospect of significantly improved mechanical properties, at least in the direction of the reinforcement. As the fibers, if continuous, must be very long and neatly ordered, one can not simply add the reinforcing material to the melt or blow it into the melt puddle, as with the particle reinforcement of rapidly solidified materials. A method must be found to introduce the reinforcing material into the melt puddle at the same rate that solid ribbon is being produced to prevent either breakage or tangling, depending on whether the ribbon is moving faster or slower, respectively, than the reinforcement.

A method was devised [31] for producing fiber reinforced metal-matrix composites, in which rapid solidification was considered a solution to the problem of undesired chemical reaction between the fiber and the liquid matrix material. This would result from the greatly reduced time for which the fibers are in contact with the matrix material in its liquid state.

In this scheme, fibers are first temporarily attached to a single chill roller in a rapid solidification apparatus (Fig. 13). When the roller was up to casting speed, the metal would be ejected onto the fibers, and the temporary attachment of the fibers to the roller broken, the fiber feed being maintained by the pulling of the solidified ribbon. Various modifications of this scheme were also proposed, such as adding a second roller for more rapid solidification and surface finishing, or adding a collimator to insure the proper placement of the fibers before they enter the melt puddle. If the metal flow and the fiber feed could be maintained, this could be a continuous process, with no theoretical limit to the length of composite ribbon produced.

No examples of suitable fiber/matrix systems were suggested by the developers of this method, so it is unclear what, if any, systems were actually attempted. Some system was

probably investigated, as it was claimed that the minimum volume fraction of fibers was reduced below the 60–70% required by the conventional method of pulling fibers through molten metal. It has been demonstrated [29], however, that it is important with this sort of apparatus, for the fibers and the matrix material be selected so that the fibers are wetted by the molten metal. If this is not the case, the metal may ride on top of the fibers and only a few chance fibers will be incorporated into the matrix.

One system in which the liquid matrix material wets the reinforcement is that of $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ ribbons reinforced with W wires. It has been shown [29] that excellent bonding can be achieved between the wire and the matrix, probably due to the good wetting of the wire by the matrix. In this case a length of 10 μm diameter wire was incorporated into a matrix using a single roller technique similar to that discussed above, except that the wire was not attached to the chill roller, but was simply draped over it while the other end was lightly fastened to a support. The motion of the first metal to solidify around the wire, imparted by the chill roller, tore the wire free and brought it forward as more ribbon was produced. The excellent quality of the fiber/matrix bond was demonstrated with bending tests, in which debonding did not occur until considerable necking had occurred. This technique can, obviously, only be used with such reinforcing media as can withstand the stress produced by being suddenly accelerated from stationary to the speed of the chill roller's surface; W wire is well-suited to this. It should be noted that this technique could not incorporate C fibers into $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$, probably due to the poor wetting of the fibers by the melt.

Further investigation of the $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ /W system [32] showed that multiple reinforcing wires could be introduced with a method that, additionally, allowed for continuous production (Fig. 14). In this scheme, the wires were pulled from a supply wheel, along the surface of a single chill roller, and wound up on a driven take-up wheel. The speed of the wire was matched to the surface speed of the chill roller. A slight resistance to

rotation of the supply wheel kept the wires taut. It also keeps them tangle-free if each wire is wound onto a separate section of the supply wheel. This method was used to produce $\text{Ni}_{75}\text{Si}_8\text{B}_{17}$ ribbon with either two 26 μm diameter W wires, one 60 μm wire, or one 10 μm wire. The single 10 μm wire, being unable to withstand the acceleration of the drive wheel by itself was incorporated into a ribbon by winding a 60 μm wire onto the supply wheel separately and attaching it to the drive wheel, passing to the side of the melt puddle, while the 10 μm wire was parallel to it, but passed through the melt puddle. The 60 μm wire, then, accelerated the supply wheel, but only the 10 μm wire was embedded in the ribbon. Examination of the ribbon with the embedded wires revealed that the ribbons sometimes split or had holes and brittle zones along the wire along the wires if the roller speed was too high and thus the ribbon too thin. Slowing the roller's surface speed down to 20 m/s eliminated these problems, but the wire(s) still protruded from the free surface (the side not in contact with the chill roller) at places. Some areas of the surface in contact with the chill roller near the wire appeared as shiny as the free surface, indicating a reduced cooling rate there, and suggesting that crystallization and embrittlement may occur. X-ray analysis showed that the boundary between the wire and the matrix was sharp, indicating that no reaction or diffusion occurred between the wire and the melt in the very short time before solidification.

5 Conclusion

Rapid Solidification is the route to many different novel composite materials. RS laminates may be produced from amorphous metallic alloys that would crystallize if hot-pressed. Reinforced RS composites may be prepared with amorphous metallic matrices and with reinforcing media that would react with the matrix material or be degraded by the temperature if prepared by conventional methods. These reinforced RS composites can have significantly improved mechanical or other properties compared to the unreinforced

matrix material. The technology for the production of discretely reinforced RS composites is reasonably well developed, but that for the production of continuously reinforced composites will require much more research before it is of practical interest. The primary limitation on the selection of reinforcing and matrix materials, both from the standpoint of production and that of properties, is the wettability of the reinforcement by the matrix. Solving this class of problems will enable more combinations of reinforcements and matrices to be used, yielding composites with improved properties tailored to their intended use.

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Figure Captions

- Fig. 1. Double roller apparatus for production of laminated RS composite ribbon [5] (courtesy S. Shimanuki).
- Fig. 2. Single roller apparatus for production of laminated RS composite ribbon [7] (courtesy S. Shimanuki).
- Fig. 3. Flat belt modification of single roller apparatus for production of laminated RS composite ribbon [6] (courtesy S. Shimanuki).
- Fig. 4. Drum interior apparatus for production of laminated RS composite ribbon [8] (courtesy R.V. Raman).
- Fig. 5. Transverse surface profile of $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$ laminated RS composite ribbon made by ejecting a narrow melt stream upon a ribbon formed from a wider melt stream [9] (courtesy H.H.Liebermann).
- Fig. 6. Apparatus for producing edge-bonded RS composite ribbon [10].
- Fig. 7. Apparatus for spray forming a metallic strip [11] (courtesy A.R.E. Singer).
- Fig. 8. Apparatus for producing a discretely reinforced RS composite ribbon by adding particles to the melt [12].
- Fig. 9. Yield stress for an amorphous $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ composite as a function of volume fraction 4–5 μm WC particles [15] (courtesy H. Kimura).
- Fig. 10. Laminar flow process for producing RS spheres in rotating water [21] (courtesy H. Kimura).

- Fig. 11 Effective permeability as a function of frequency for a $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ ribbon reinforced with 1% WC particles by volume, compared with an unreinforced $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ ribbon, both annealed for 5 min at 723 K [22] (courtesy H. Kimura).
- Fig. 12. Apparatus for producing a discretely reinforced RS composite ribbon by blowing particles into the melt puddle [27].
- Fig. 13. Apparatus for producing continuously reinforced RS composite ribbon by attaching reinforcing elements such as fibers or wires to chill roller [31].
- Fig. 14. Apparatus for producing continuously reinforced RS composite ribbon by pulling reinforcing elements such as fibers or wires across chill roller surface [32].

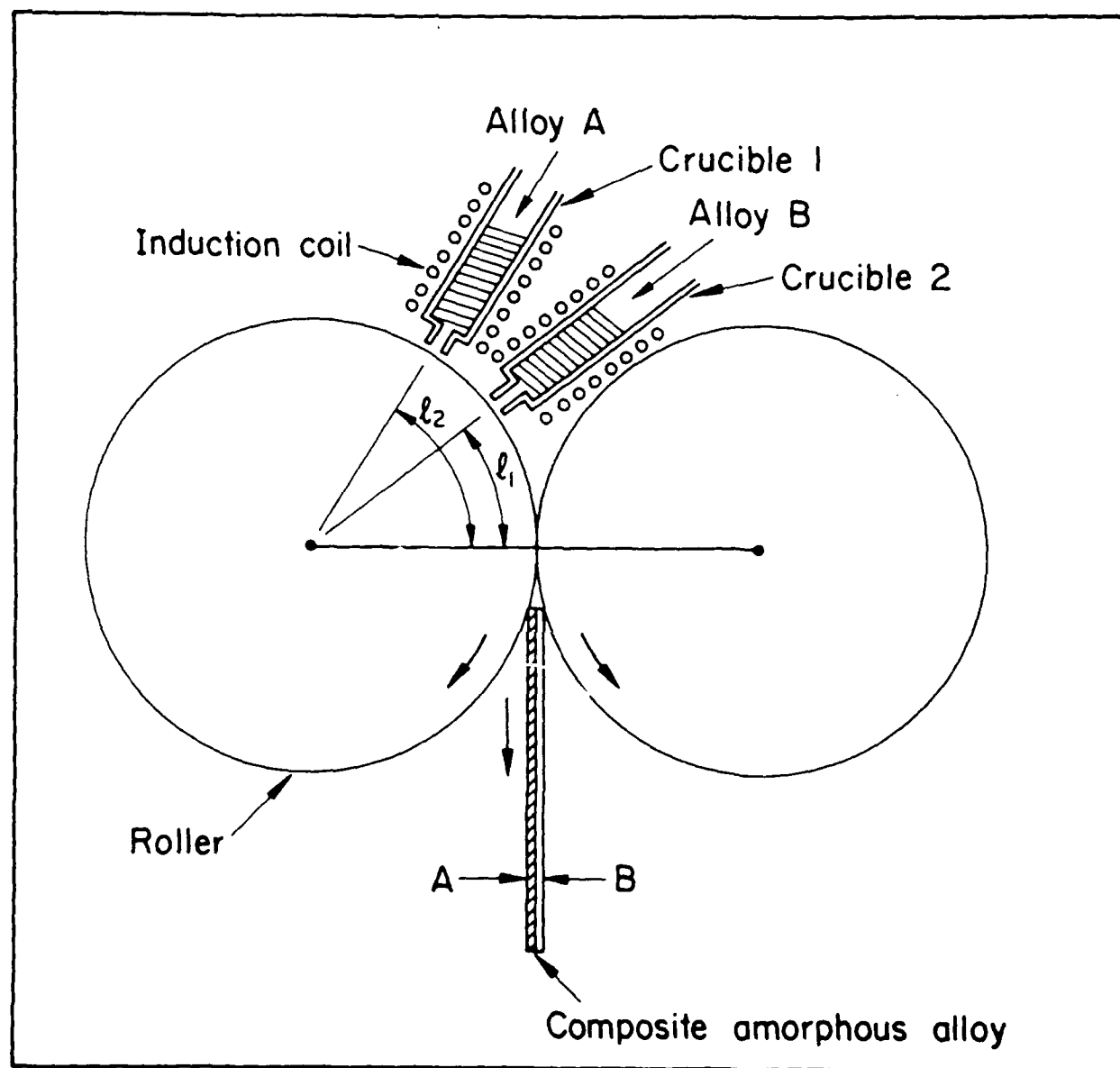


Fig. 1. Double roller apparatus for production of laminated RS composite ribbon [5]
(courtesy S. Shimanuki).

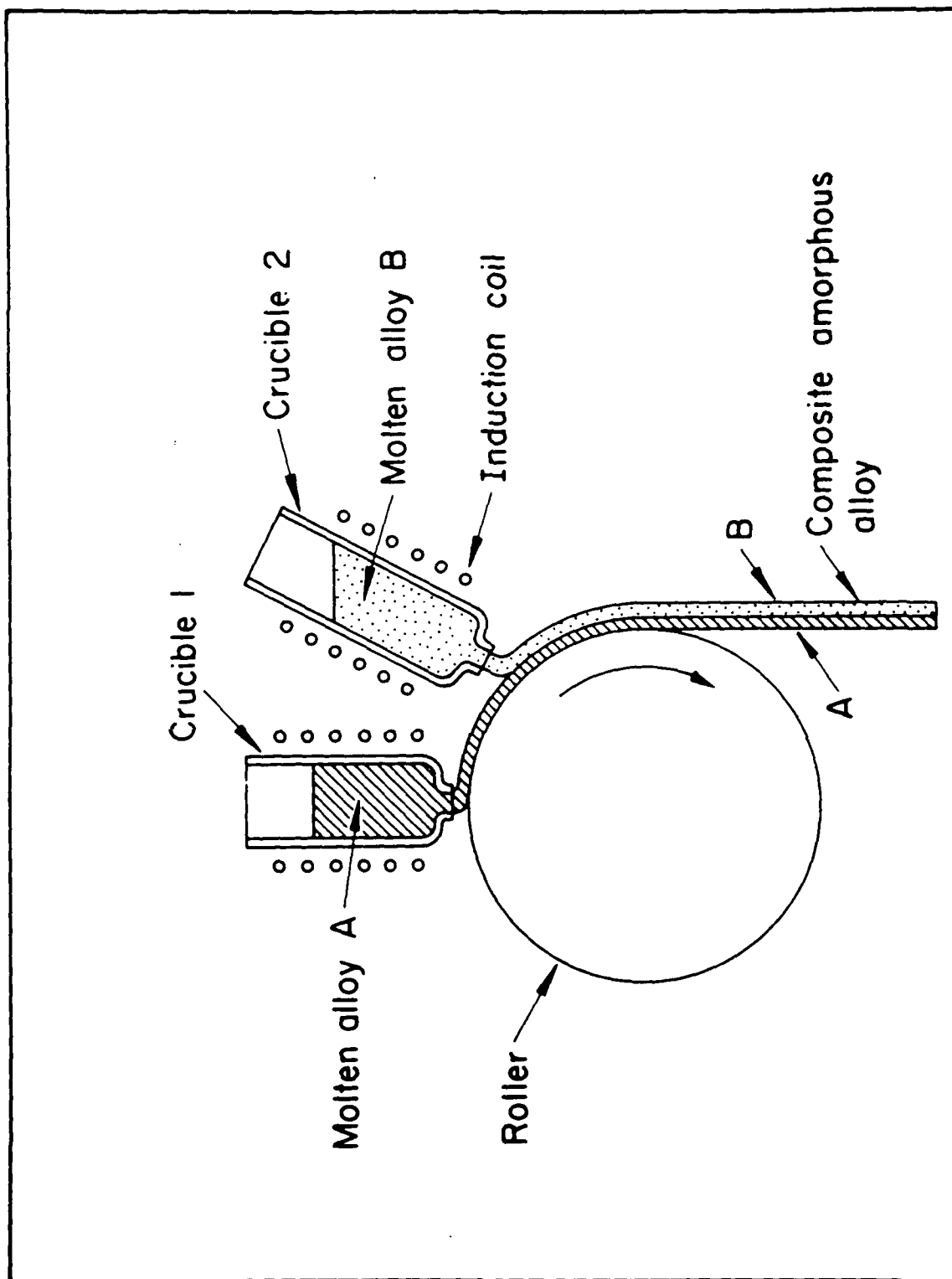


Fig. 2. Single roller apparatus for production of laminated RS composite ribbon [7]
(courtesy S. Shimanuki).

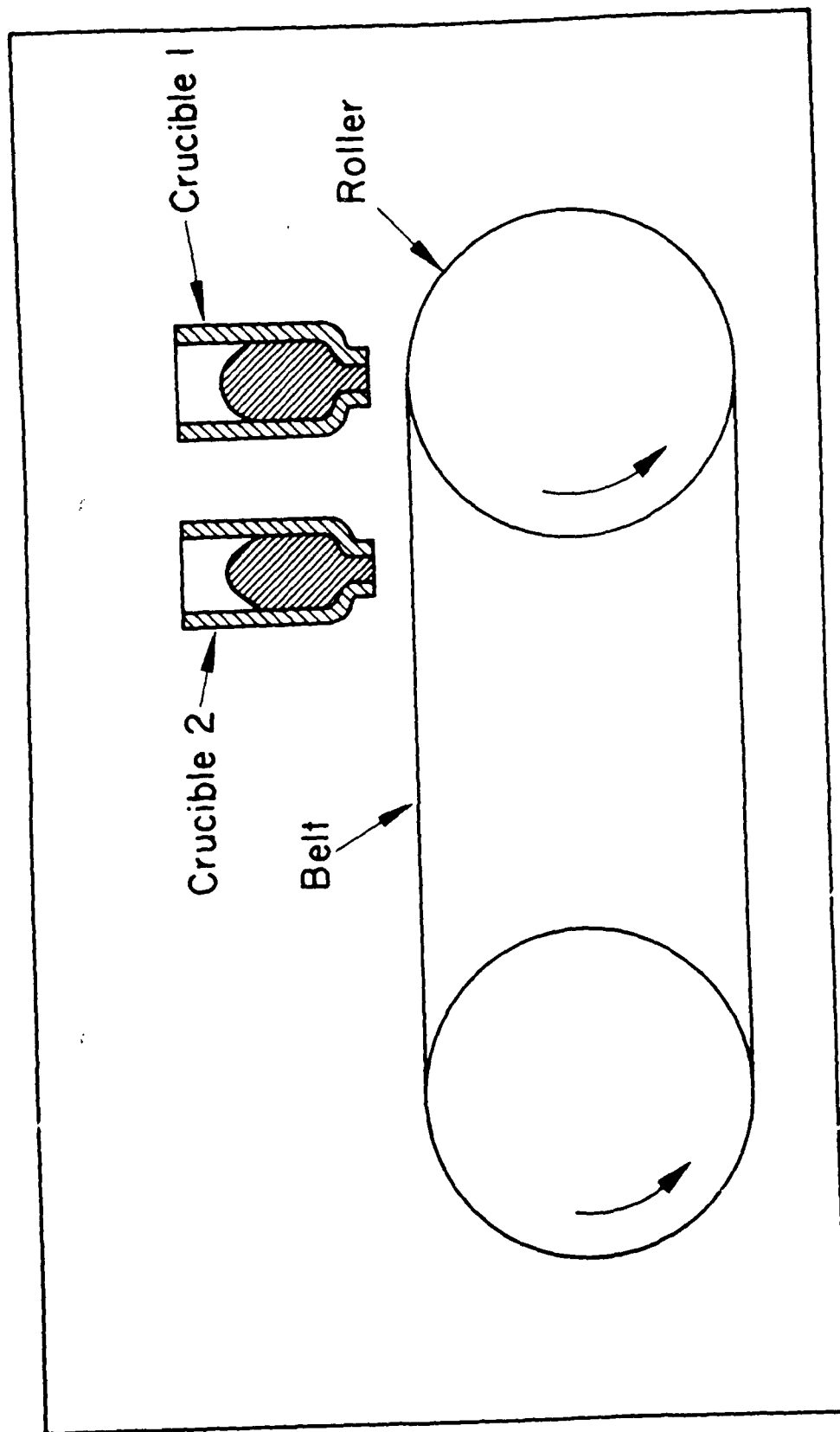


Fig. 3. Flat belt modification of single roller apparatus for production of laminated RS composite ribbon [6] (courtesy S. Shimanuki).

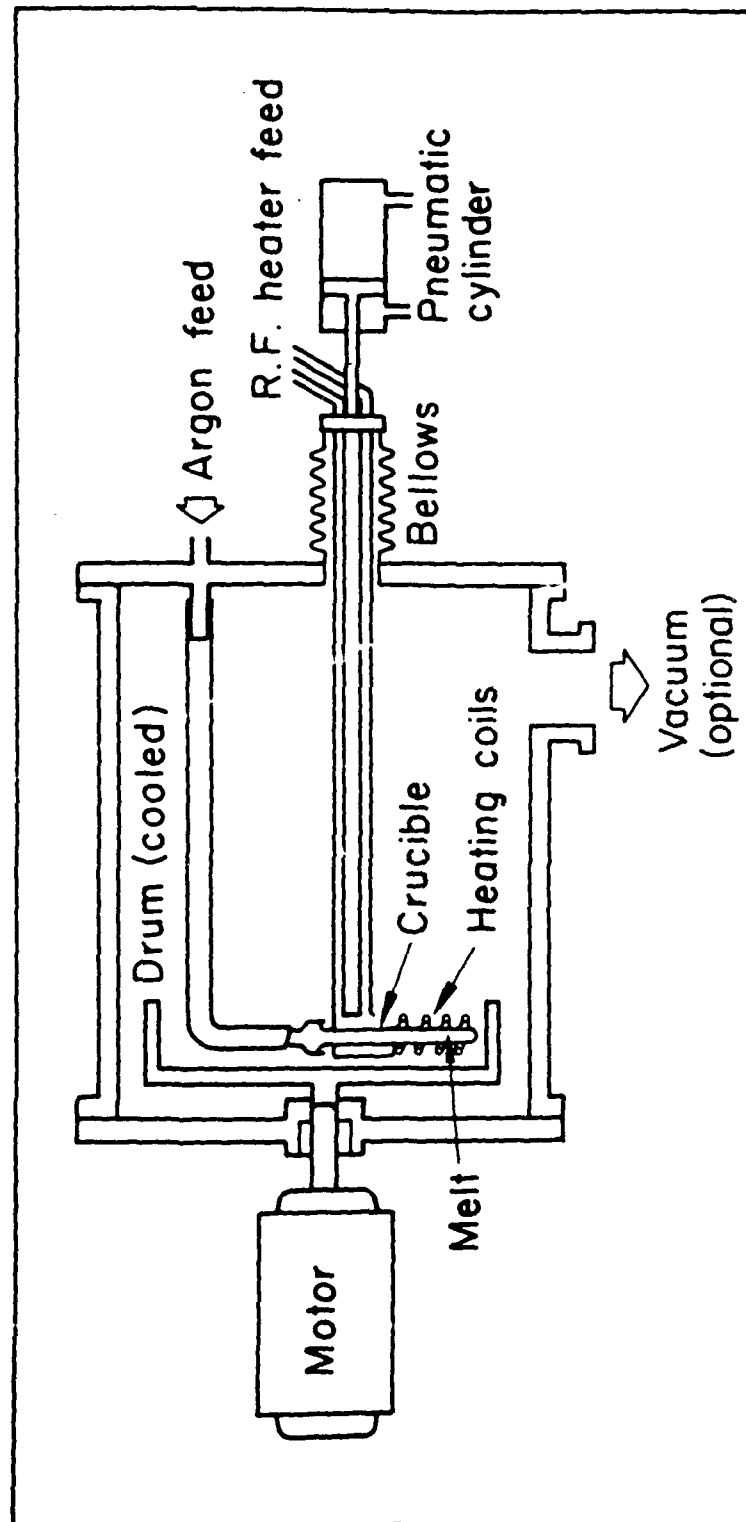


Fig. 4. Drum interior apparatus for production of laminated RS composite ribbon [8]
(courtesy R.V. Raman).

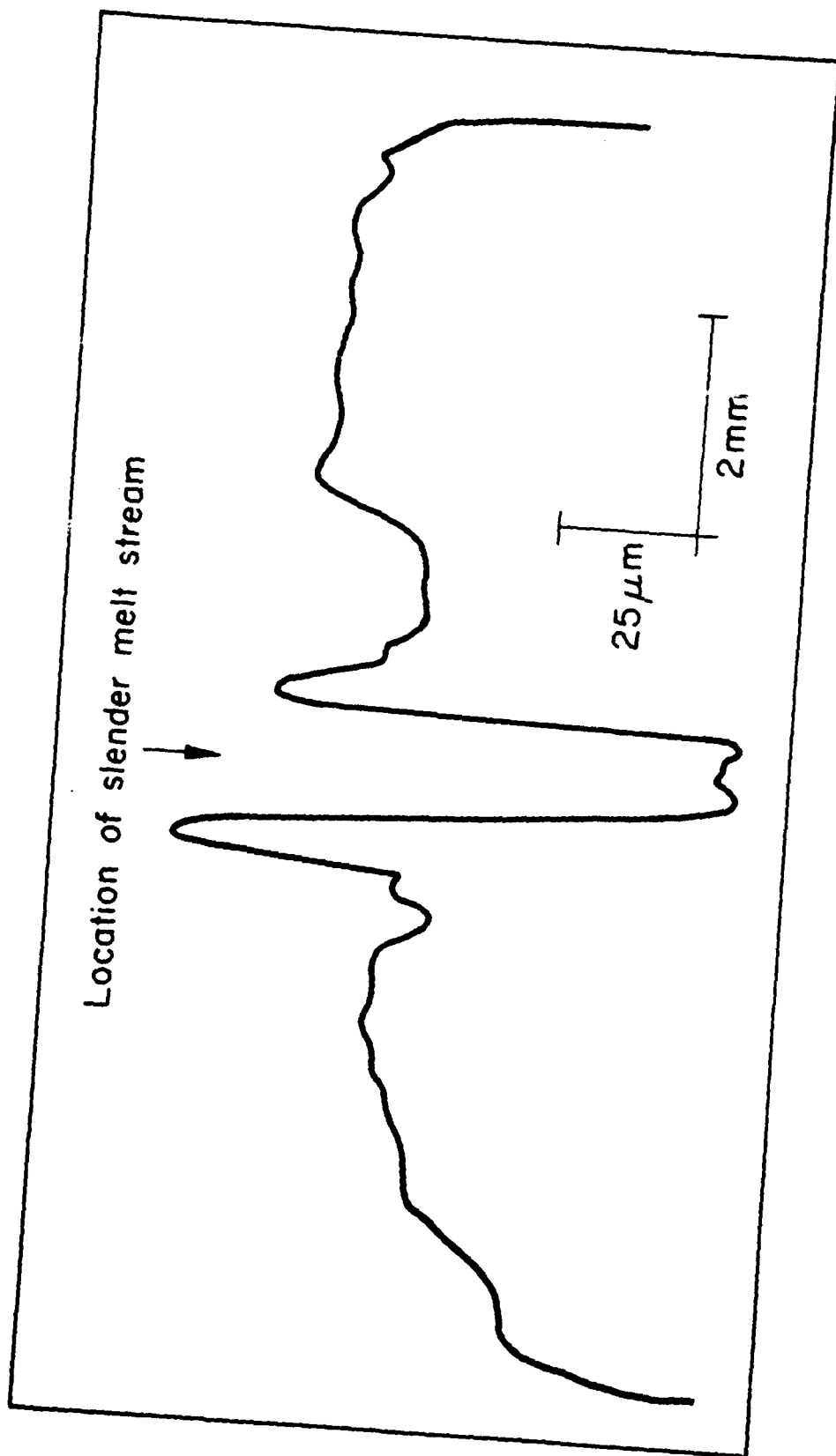


Fig. 5. Transverse surface profile of $\text{Fe}_{81.5}\text{B}_{14.5}\text{Si}_4$ laminated RS composite ribbon made by ejecting a narrow melt stream upon a ribbon formed from a wider melt stream [9] (courtesy H.H.Liebermann).

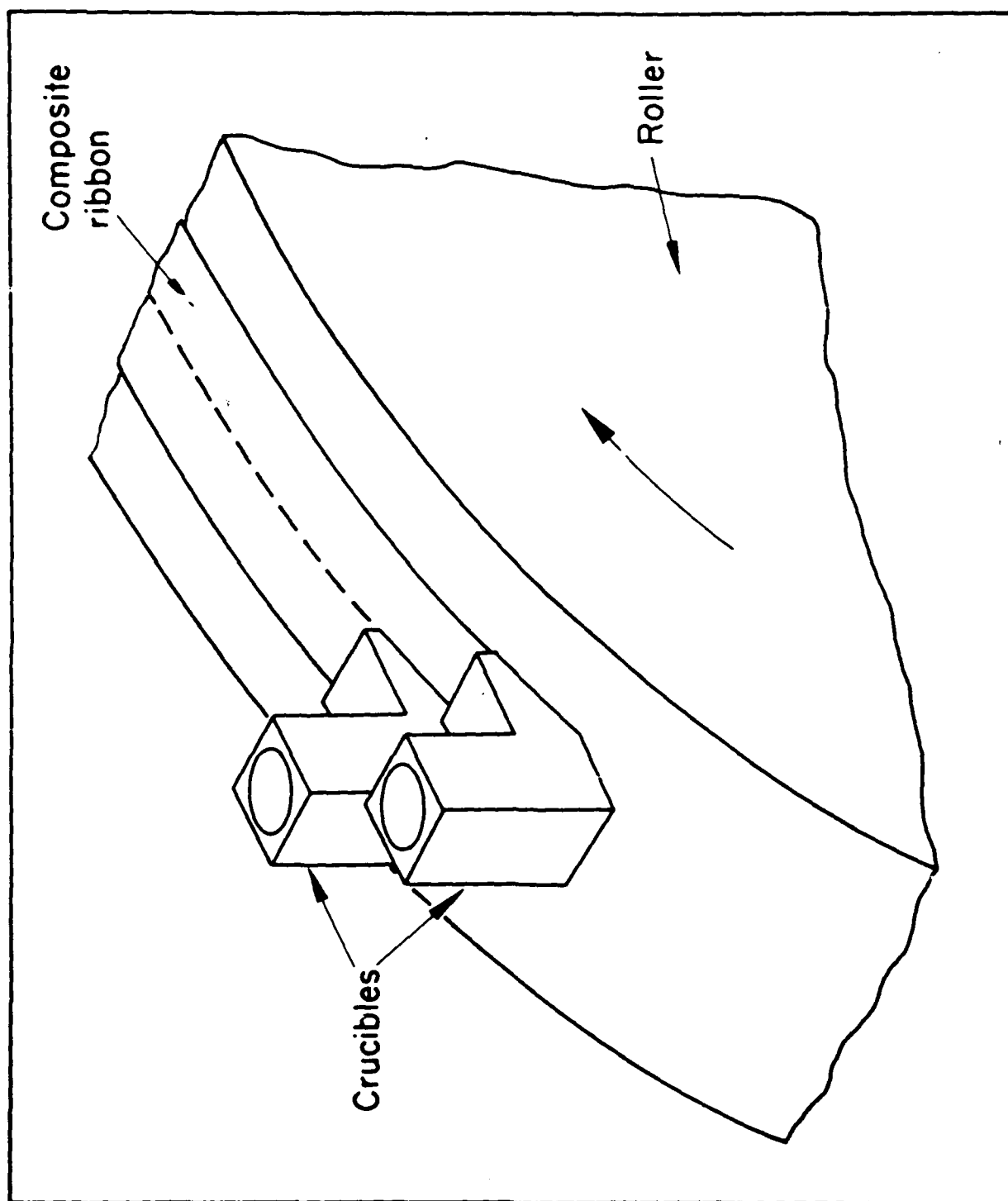


Fig. 6. Apparatus for producing edge-bonded RS composite ribbon [10].

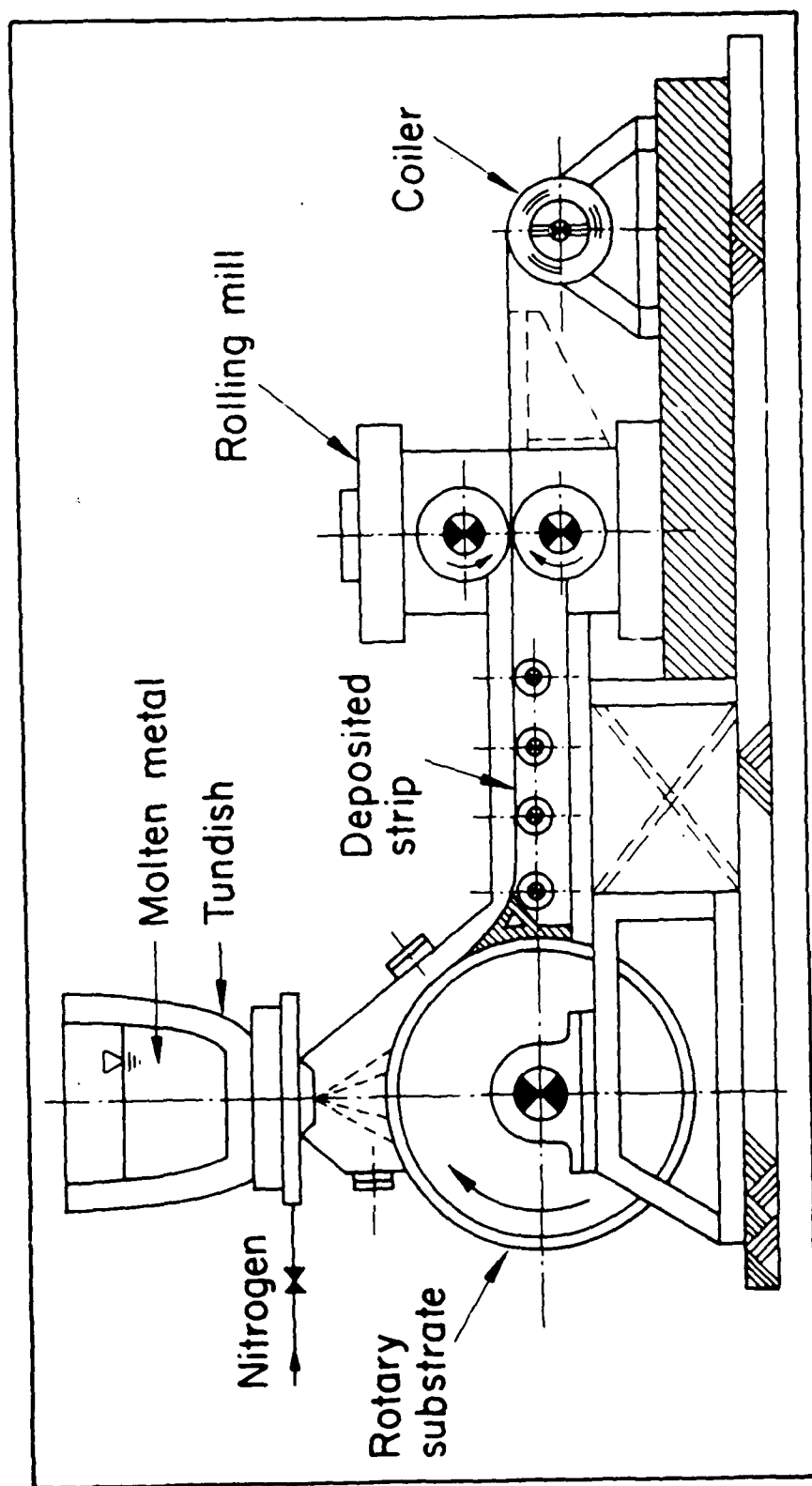


Fig. 7. Apparatus for spray forming a metallic strip [11] (courtesy A.R.E. Singer).

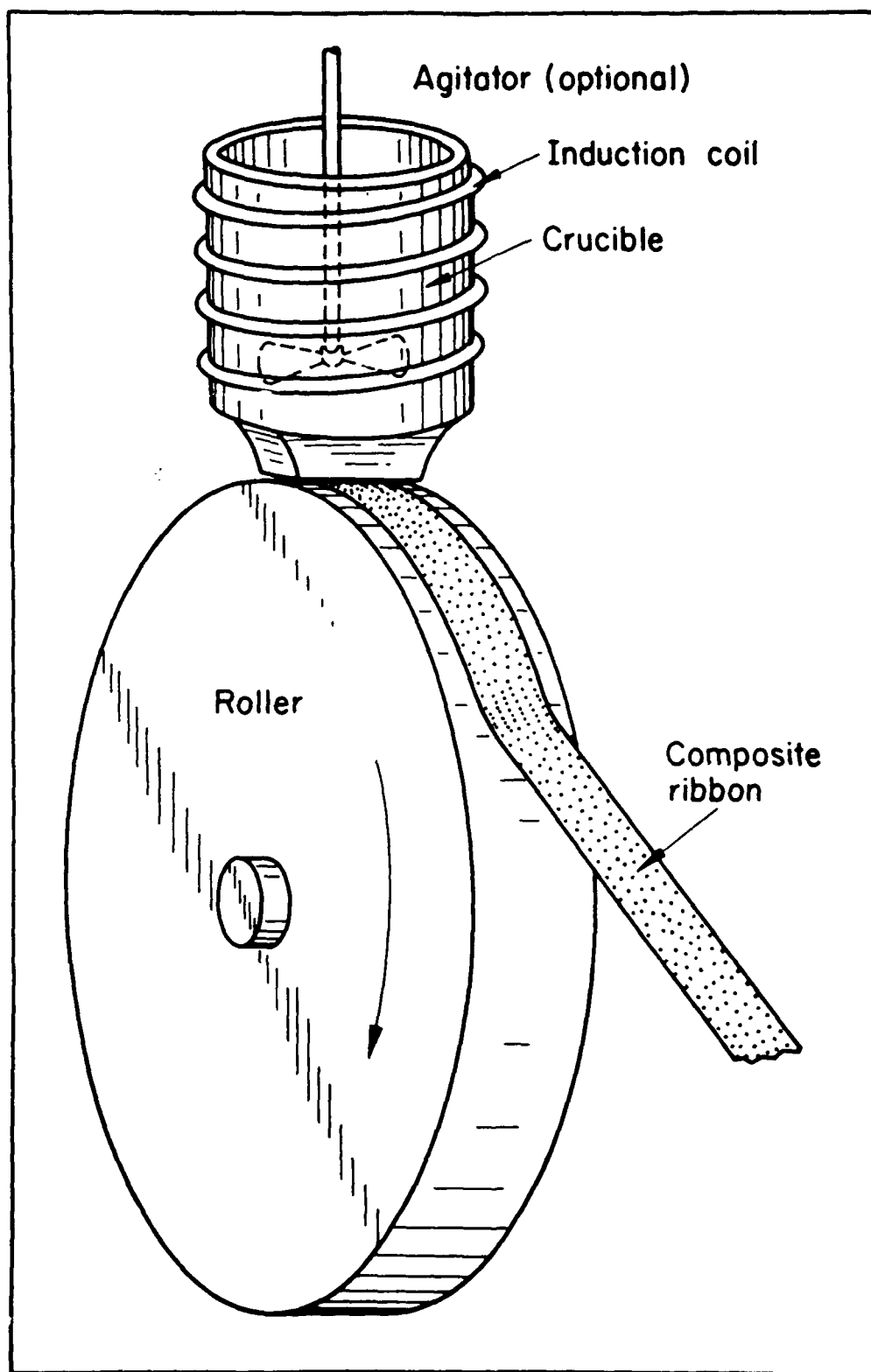


Fig. 8. Apparatus for producing a discretely reinforced RS composite ribbon by adding particles to the melt [12].

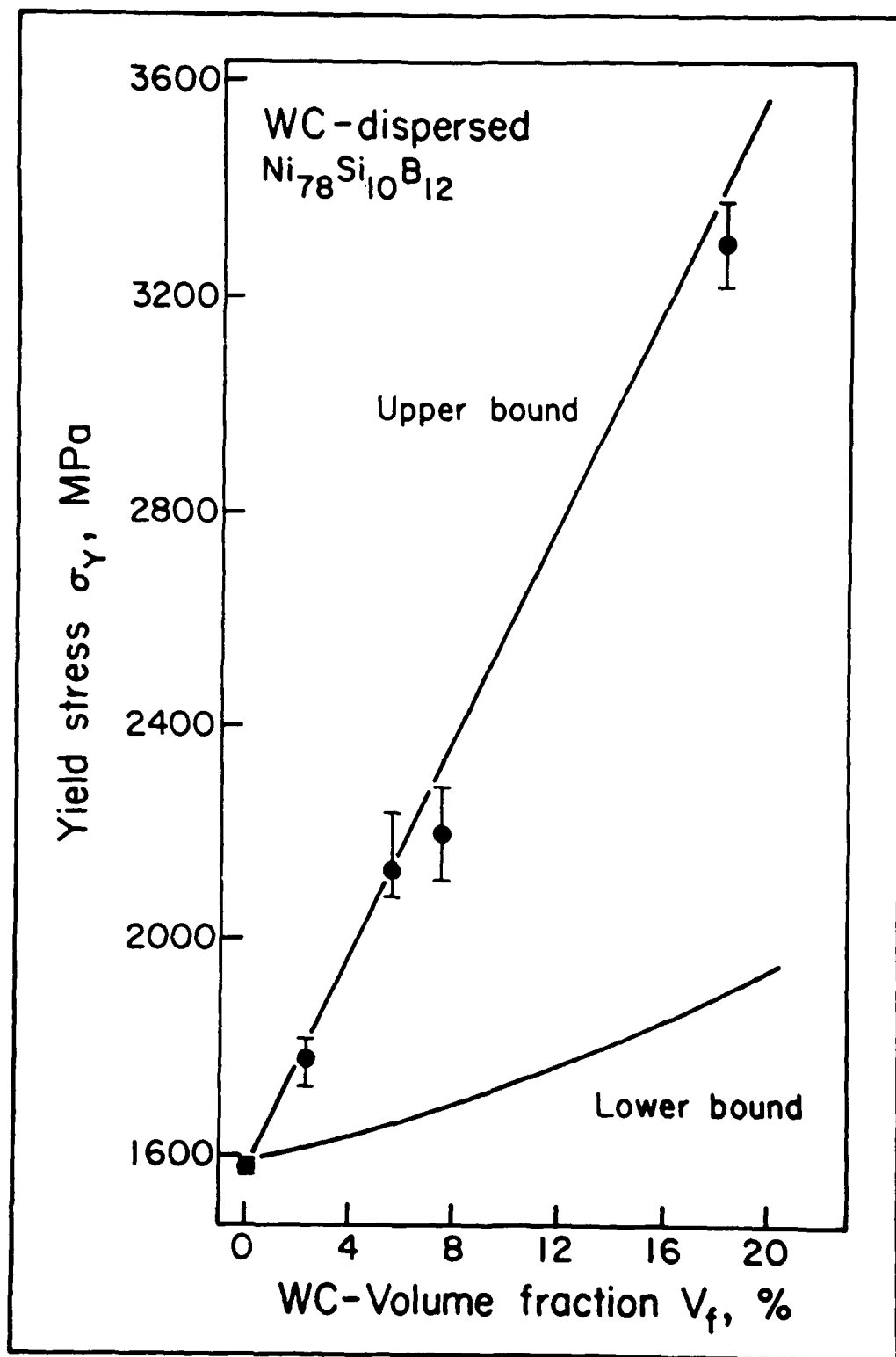


Fig. 9. Yield stress for an amorphous $\text{Ni}_{78}\text{Si}_{10}\text{B}_{12}$ composite as a function of volume fraction 4-5 μm WC particles [15] (courtesy H. Kimura).

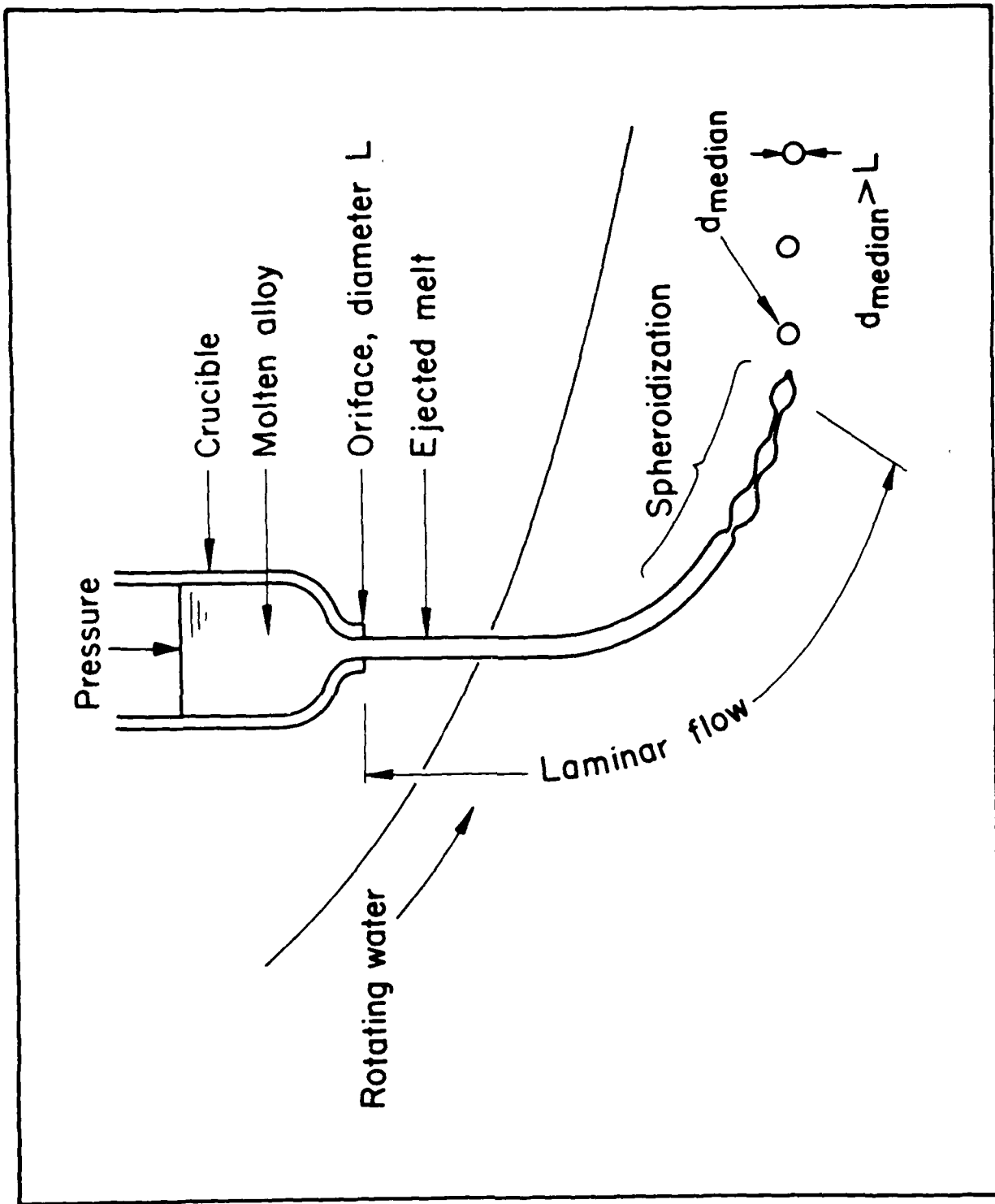


Fig. 10. Laminar flow process for producing RS spheres in rotating water [21] (courtesy H. Kimura).

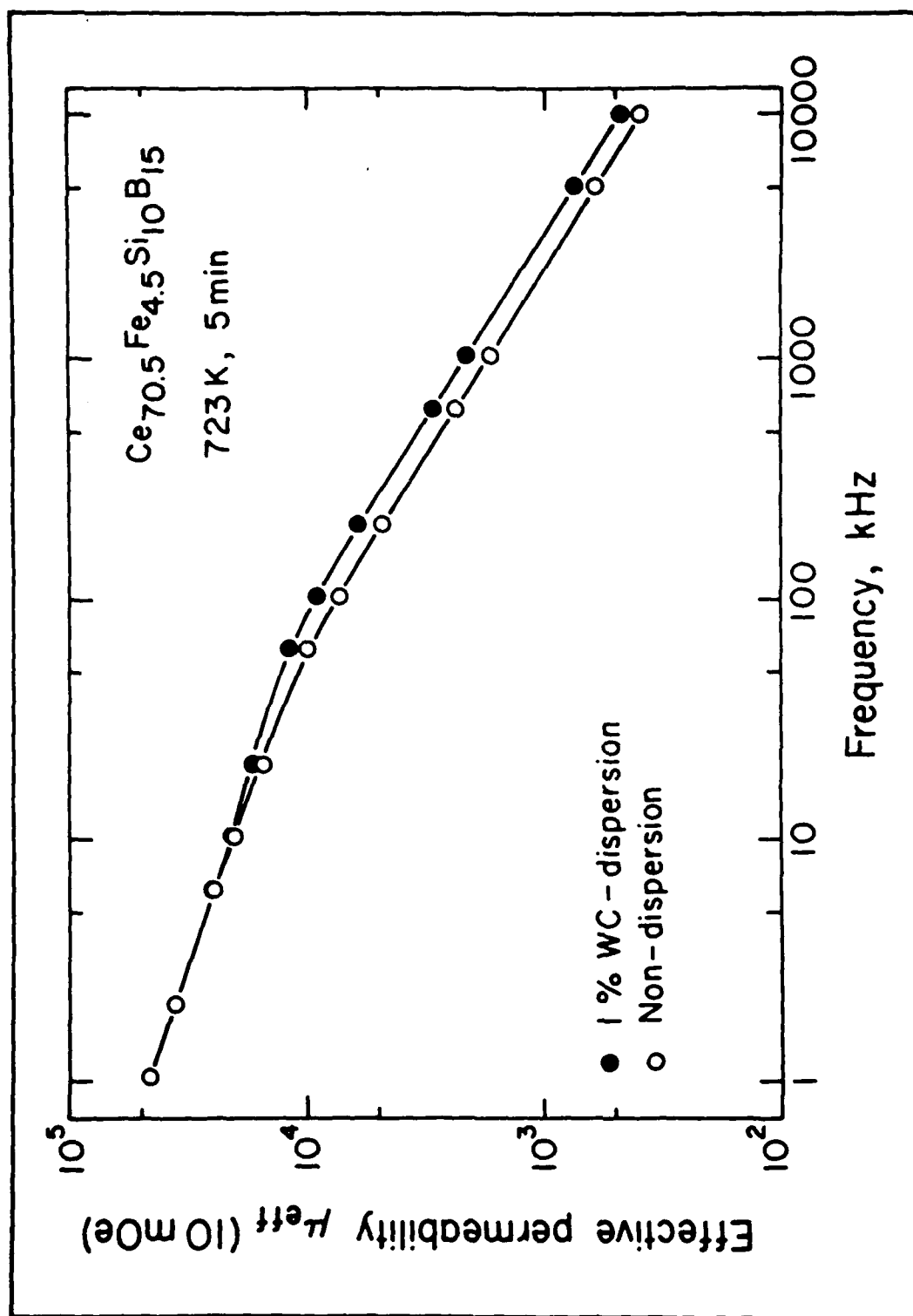


Fig. 11. Effective permeability as a function of frequency for a $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ ribbon reinforced with 1% WC particles by volume, compared with an unreinforced $\text{Co}_{70.5}\text{Fe}_{4.5}\text{Si}_{10}\text{B}_{15}$ ribbon, both annealed for 5 min at 723 K [22] (courtesy H. Kimura).

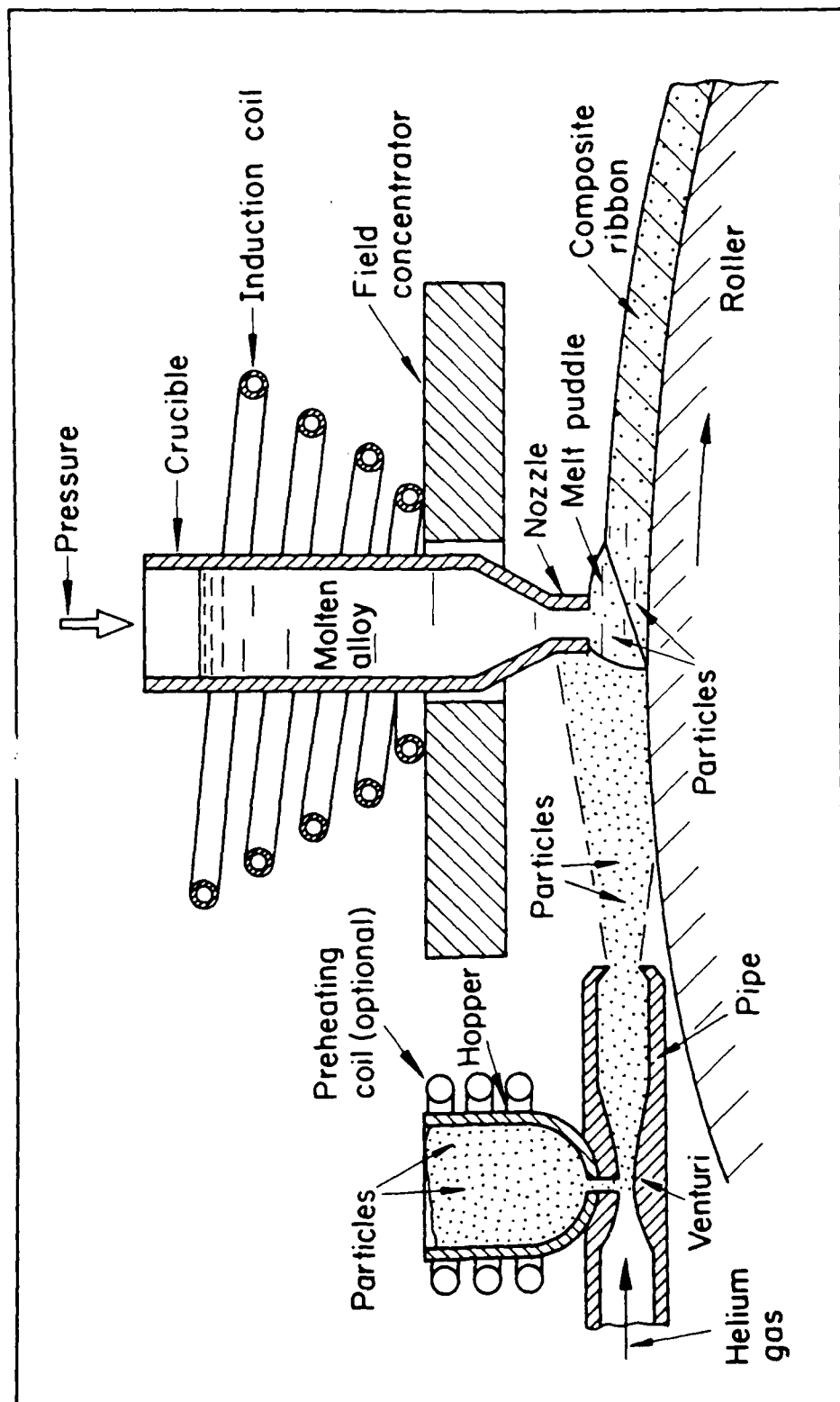


Fig. 12. Apparatus for producing a discretely reinforced RS composite ribbon by blowing particles into the melt puddle [27].

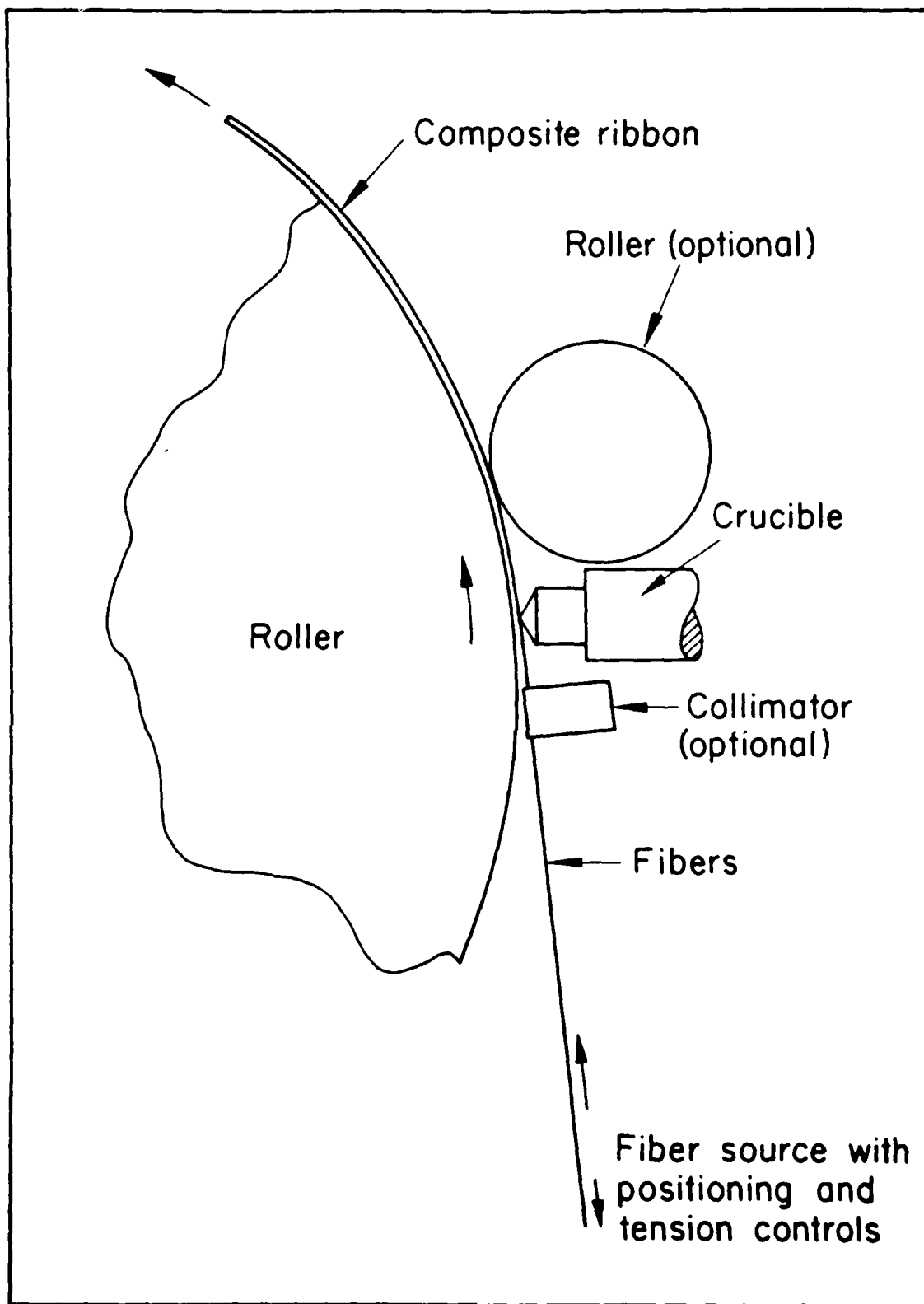


Fig. 13. Apparatus for producing continuously reinforced RS composite ribbon by attaching reinforcing elements such as fibers or wires to chill roller [31].

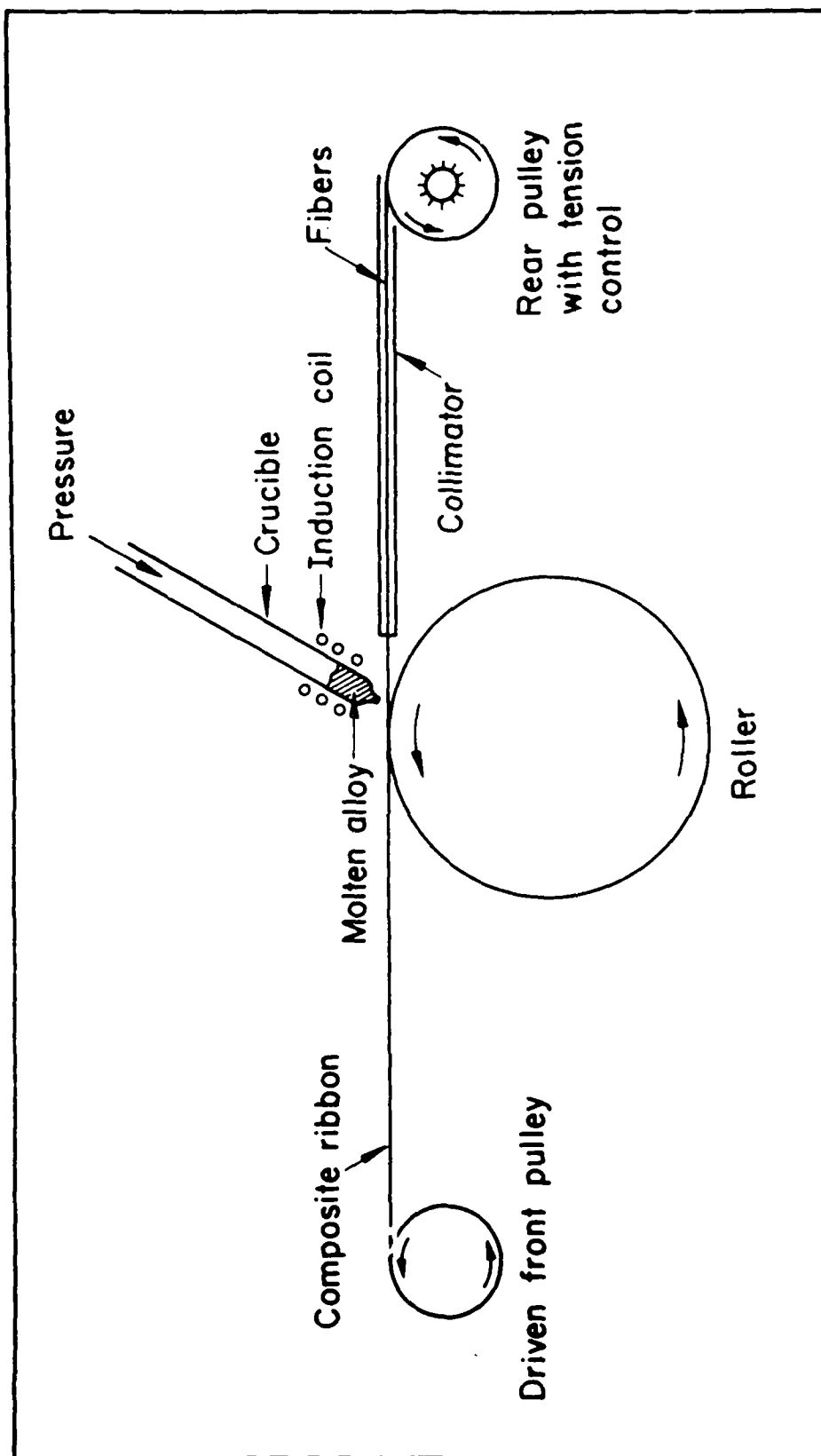


Fig. 14. Apparatus for producing continuously reinforced RS composite ribbon by pulling reinforcing elements such as fibers or wires across chill roller surface [32].